Design, synthesis, morphology and properties of semiconducting block copolymers for photonic applications

de Boer, Bert

Chapter 1

Introduction

Abstract

A brief historical overview of the developments and breakthroughs of semiconducting polymers and their applications is given, and the concepts and current understanding of photovoltaic devices and light-emitting diodes is presented. The influence of the morphology on the performance of the opto-electronic devices is outlined and the approach of using semiconducting block copolymers is introduced. The advantages of using block copolymer in terms of morphological control on the nanometer scale are stressed and the synthetic approach that utilizes "living' free radical polymerization techniques to obtain semiconducting block copolymer is presented. The challenges and problems of organic/metal and organic/organic interfaces are introduced and by using energy diagrams, the differences between photovoltaic devices and light-emitting diodes, are schematically depicted. Finally, the aim and outline of this thesis are presented.

1.1 Semiconducting polymers and their applications

Traditionally polymers have been associated with insulating properties in the electronic industry and are applied as insulators of metallic conductors or photoresists. Since the serendipitous discovery in 1977 of the doping of polyacetylene, which resulted in increasing the conductivity of polyacetylene by eleven orders of magnitude,[1,2] many academic and industrial research laboratories initiated projects in the field of conducting polymers. Although the initial emphasis was on the conduction properties obtained by doping of conjugated polymers, since over a decade the research has focused on soluble and intrinsically (semi)conducting polymers. In the 25 years that have elapsed, many novel materials were designed, synthesized and developed for their specific physical or chemical properties and implemented in a variety of applications.

In 1990 the Cambridge group reported emission of light from a plastic sandwich that was connected to a battery.[3] The discovery of electroluminescence (EL), i.e., the emission of light upon excitation by the flow of electric current, in conjugated polymers has provided a new impetus to the development of light-emitting diodes (LEDs) for display and other applications.[4] In LEDs, the injected holes and electrons recombine and produce luminescence with a wavelength (color) that depends on the energy difference between the excited state and the molecular ground state. For the majority of conjugated polymers, electron injection is more difficult than hole injection, since the majority of conjugated polymers are more easily oxidized than reduced. Using metals with a low work function (e.g. calcium) as the cathode material has remedied this. However, calcium is highly susceptible to atmospheric degradation and should therefore be encapsulated by a metal that is not sensitive towards oxygen and moisture, like aluminum. With the appropriate choice of polymer and device design, external efficiencies of up to 4 % can be obtained, which is comparable with the best EL devices based on inorganic materials. Turn-on voltages of 5 V or below have also been achieved by the use of charge-transporting layers, enabling devices to be run from low-power sources like batteries.

Polymer-based electroluminescent displays provide a good alternative to the well-established display technologies based on cathode-ray tubes and liquid-crystal displays (LCDs) with respect to processability and viewing-angle. Especially for the application in large-area displays and flexible displays, for which the conventional methods are not well suited, polymer light-emitting diodes (PLEDs) offer great advantages.

Two years after the breakthrough in Cambridge, the Santa Barbara group reported the first results on polymer-based photovoltaic cells,[5,6] the principles of which can be regarded as the inverse of the EL process. In photovoltaic devices (PVDs), a bound electron–hole pair (exciton) is created upon illumination, which needs to be dissociated into separate charges that must be driven out by the built-in potential field between two electrodes with different work functions. To dissociate the exciton, the concept of electron donor and acceptor is frequently used, in which the electron affinity of the electron acceptor

should be larger than the ionization potential of the donor.[7] Since the first publications, most PV cells are based on blends of poly(*p*-phenylene vinylene) (PPV) derivates and C_{60} as light absorber/electron donor/hole conductor and electron acceptor/electron conductor, respectively, a combination which has proven promising.[8,9] PPV-based materials are widely investigated for their opto-electronic properties[10–13] and the ability of C_{60} to accept several electrons[14] makes it a particularly attractive material for the use as electron acceptor. Its low solubility is a major drawback, however. A way to overcome this is the functionalization of C_{60} with side-chains or the incorporation of C_{60} into polymers, thus yielding materials that combine the physical properties of fullerene with the processability of polymers.[15,16]

Upon irradiation of an organic PVD, an exciton is created in the PPV phase, which is followed by a very rapid electron transfer (< 200 fs)[17] to the C_{60} phase (photoinduced electron transfer). Since all other known competing relaxation processes in conjugated polymers occur on time scales that are orders of magnitude larger, this ultra-fast charge transfer must have a quantum efficiency of approximately unity, i.e., nearly all excitons that are created near the donor–acceptor (D–A) junction are transferred to the C_{60} phase. Despite the high electron transfer efficiency, the power conversion efficiency of polymer/fullerene-based photovoltaic devices is typically still in the range of one percent due to the low mobility of holes on the conjugated polymer and the formation of a non-continuous pathways for the charges, which results in an inefficient collection of charges at the cathode and anode, respectively.[18] Recently, power conversion efficiencies of 2.5–3 % were reported for mixtures of substituted PPV and C_{60} solution-processed from chlorobenzene.[19,20]

The importance of the field of semiconducting polymers was recently stressed by awarding the 2000 Nobel prize in chemistry to the discoverers Heeger, Shirakawa and MacDiarmid. Since the last decade the research has focused on the applications of soluble and intrinsically semiconducting polymers as active material in field-effect transistors,[21–23] light-emitting diodes,[3,10,24–26] photodetectors,[27] photovoltaic cells,[5,6,28,29] sensors[30] and lasers (solution[31,32] and solid-state[33–37]). In addition to the good performance of the material in these devices, they also provide a way towards patterned structures by inexpensive techniques such as spin casting, photolithography,[38,39] ink jet printing,[40–42] soft lithography,[43] screen printing[44] and micromolding[45] onto almost any type of substrate, including flexible ones.[46]

1.2 Structural organization in block copolymers

In recent years, the demand for advanced organic materials with new properties has sparked the development of novel and innovative synthetic methods that allow one to implement the desired functionality in a predictable and controllable way. Since many of these functional materials are of a composite nature, some structural organization is usually required for the material to efficiently perform its function. The organization may vary,

from simple dispersion with a proper domain size to preferential alignment, periodicity, asymmetry, etc. For the creation of the necessary structural order, with structural elements covering a wide range of length scales, concepts from supramolecular organic chemistry have been applied with great success.[47–49] Meanwhile, the now classical phenomenon of microphase separation in block copolymers[50–52] may also be exploited to realize self-structuring.[53,54] The chemical connectivity between the blocks forces the self-structuring to be on the same scale as the radius of gyration of the macromolecules, i.e., on a scale of 10–50 nm. For the simplest case, that of fully flexible (coil–coil), non-crystallizing diblock copolymers, phase separation sets in when χN exceeds a critical value; χ represents the interaction enthalpy and N the degree of polymerization (entropy factor). A set of semi-continuous and co-continuous two-phase morphologies has been identified. The stability limits of these morphologies depend primarily on the block length ratio. Actual structures obtained may not represent thermodynamic equilibrium and will depend on the phase separation mechanism and on kinetic factors of mass transport. The phase diagram is different for rod–coil block copolymers,[55–57] or when (liquid-) crystalline domains are involved.[58,59] It is generally accepted that the χ parameters in liquid-crystalline block copolymer systems are much larger than for conventional coil–coil block copolymers due to mesophase formation.[60] Only limited information has been gathered about these more complicated systems, so far. Similarly, the more involved and diverse morphologies found for triblock copolymers remain largely unexplored (see, e.g., Reference 61).

Examples of multi-component materials that could benefit from morphological structuring are the active layer of a photovoltaic cell or a polymer light-emitting diode. In the photovoltaic devices, the active thin film is a composite of electron-donor molecules and electron-acceptor molecules, between dissimilar electrodes (for instance, Aluminum (Al) and indium–tin oxide (ITO)).[62,63] The performance of this type of device is very sensitive to the morphology of the active layer. Obviously, both the donor and the acceptor phases should form a continuous path to their electrode to allow bipolar charge transport. Ideally, to ensure efficient exciton dissociation, an acceptor species should be within the exciton diffusion range from any donor species, and vice versa. Since the exciton diffusion range is typically several nm, and therefore shorter than the light absorption depth (~100 nm), the convoluted donor–acceptor interface of an interpenetrating morphology[63–65] should be more efficient in terms of exciton dissociation than a planar double-layer structure. In the optimized morphology, the characteristic size of the channels of the phases is matched to the exciton diffusion range. In principle, structuring on this scale may be achieved through phase separation in diblock copolymer films.

Besides this particular case of a photovoltaic material that requires the availability of a copolymer of suitable donor and acceptor blocks, also polymeric material for light-emitting diodes can greatly benefit from control over the morphology through microphase separation. In PLEDs, charges have to be injected into the active polymer material (Section 1.4) and transported through the polymer in order to recombine. Recombination of charges should take

place in materials with high electroluminescence efficiency such as PPVs. Unfortunately PPVs do not conduct electrons very well, but can be utilized as the hole transporting material. Consequently, the function of PPV is two-fold, namely to operate as hole transporting layer and as electroluminescent material. To ensure effective recombination of the both charges (balanced charge transport), the active material should have the capability of transporting electrons as well as holes. Organic materials with electron deficient groups such as oxadiazoles are known to have relative good electron mobilities and can, therefore, be used as the electron-transporting phase in PLEDs. Although the use of blends of PPV with electron-transporting materials has been applied,[24] mixing of both components will most probably lead to macrophase separation and result in a small interfacial area between the electron- and hole-transporting phases, which is, in turn, detrimental to the recombination efficiency of the positive and negative charges. Therefore, microphase separation of bifunctional block copolymers consisting of an electron-transporting and a hole-transporting/light-emitter block can be very advantageous for controlling the structural ordering in PLEDs.

1.3 Controlled radical polymerization technique

According to the principles laid out above, self-structuring in photovoltaic devices and in light-emitting diodes may be achieved through a diblock copolymer consisting of a PPV block and a block densely functionalized with C_{60} or oxadiazoles, respectively. For the formation of block copolymers, a large array of synthetic strategies is available to the chemist. The most prominent of these is living anionic polymerization.[66] This method yields products with very low polydispersities, but it has its drawbacks. One is the necessity to work under very strict conditions to avoid impurities such as water and oxygen. Moreover, the highly reactive carbanion prohibits the use of various functional groups.[67] Recently, this has been overcome to some extent by the development of the controlled/"living" radical polymerization techniques.[68] Four "living" free radical polymerization methods are often employed, namely, one based on stable nitroxide counter radicals[69,70] (nitroxide-mediated "living" radical polymerization, NMRP), atom transfer radical polymerization (ATRP),[71] reversible addition-fragmentation chain transfer (RAFT)[72–74] and initiator–chain transfer–termination (iniferter).[75] The first two techniques employ the principle of an equilibrium between a low concentration of active radicals and a rather large number of dormant species. This suppresses bimolecular side reactions such as recombination or disproportionation to such a degree that the overall polymerization process shows "living" characteristics. The last two techniques (RAFT and iniferter) are based on the formation of a reactive radical and a relatively stable counter radical, where the latter does not participate in the *ini*tiation, but merely acts as a trans*fer* agent and *ter*minating species *(iniferter*). In the case of RAFT, additional conventional initiators (AIBN, BPO) are used to start the polymerization, in which a dithio-compound is utilized as a very efficient reversible chain-transfer agent. The chain-transfer agent is constantly

transferred from one active radical to another, leading to a low concentration of active radicals, which suppresses the bimolecular side reactions. Although the iniferter technique is not as efficient in producing polymers with very low polydispersities as the other three techniques, it has the advantage of performing "living" free radical polymerizations upon initiation by UV-light (photopolymerization at 365 nm).[75–77]

The advantages of "living" free radical polymerizations are (a) linear increase of molecular weight with time, (b) possibility of the formation of block copolymers by reinitiating the polymerization in a different monomer solution, and (c) compatibility with a wide variety of monomers, e.g., acrylates, styrenes, acrylonitrile, and derivatives. Furthermore, in the particular case of surface-initiated "living" free radical polymerizations, the preparation and handling of the samples are easier,[78] which allows one to characterize the surface between two subsequent polymerizations (Chapter 7).

1.4 Interfaces and interface/surface modifications

The investigation of the interfacial electronic structure forms one important aspect for understanding and improving the performance of devices like PLEDs and PVDs. In particular, the organic/metal and organic/organic interfaces have attracted much interest in relation to performance. The properties of the interfacial electronic structure have been very well studied by surface-sensitive techniques like ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), photoemission yield spectroscopy (PEYS), etc. For this purpose, very thin films, often monolayers, of low molecular weight model compounds are vapor-deposited on metals under ultra-high vacuum (UHV). Spectroscopic investigations under UHV demonstrated the occurrence of band bending at the organic/metal interface and alignment of the energy levels at the interfaces. Caution should be exercised in using the results obtained in ultra-clean environments to explain phenomena observed in polymer-based device configurations. The electronic properties of polymer-based devices are significantly affected by the atmosphere, in which the devices are prepared or used. Generally, polymer-based devices are prepared by casting techniques with the use of organic solvent. Hence, the polymer/metal interface is not as well-defined as the organic/metal interface obtained under UHV.

For collection (injection) of holes in PVDs (PLEDs), indium–tin oxide (ITO) is most commonly used as the anode, which exhibits a high work function (4.5–5.3 eV)[79] close to the HOMO-level of the conjugated polymers. Furthermore, ITO is transparent for the visible spectrum, allowing the transmission of generated (incoming) light out of (into) the sandwiched device. For collection (injection) of electrons, a low work function metal such as Al (4.3 eV) is used as a cathode. Electron collection (injection) can be improved to some extent by using cathodes with a lower work function (Mg, 3.7 eV; Ca, 2.9 eV), but these cathodes have the disadvantage of being more susceptible to oxidation.

Early work on PLEDs was based on sandwiching a PPV-type polymer (single layer) between dissimilar electrodes, but it became evident that electron injection was very inefficient due to the energy barrier between the work function of the metal and the lowest unoccupied molecular orbital (LUMO) of PPV. Furthermore, as a result of the high injection barrier, recombination of charges occurred close to the metal-on-organic interface, and, consequently, the metal could acts as a quencher of the electroluminescence. Therefore, researchers switched to a double layer device consisting of PPV with a high-electron affinity or another electron transporting polymer e.g. based on oxadiazoles cast on top of a more commonly used PPV.[80] The introduction of an appropriate electron-transporting layer not only lowers the charge injection barrier, but it can create an energy offset for holes at the emissive layer/transport layer interface. This energy offset effectively blocks the hole current at the interface and results in a positive space-charge interfacial zone in the emissive layer. The space-charge zone will increase the field over the electron-transporting layer resulting in enhanced electron-injection from the cathode.

Figure 1.1A shows the schematic energy diagram of an organic single-layer LED in which the holes (h^+) and electrons (e^-) are injected in the highest occupied molecular orbital (HOMO) and in the (LUMO), respectively. Figure 1.1B depicts a double-layer electroluminescent (EL) device in which electrons and holes are injected from the electrodes into the electron transport layer (ETL) and hole transport layer (HTL), respectively. These carriers recombine to form an exciton that will radiatively decay (emit light). In this geometry, the interfaces consist of metal/ETL, ETL/HTL and HTL/ITO.

In PVDs, single-layer devices (Figure 1.1C) were not very efficient and in order to separate the charges efficiently, the concept of donor and acceptor was introduced[5,6] and double-layer devices, similar to double-layer LEDs, with electronegative polymers (electron acceptors) were investigated (Figure 1.1D).[81] Because the exciton dissociates only in the vicinity of the donor–acceptor interface, double layer PVDs still exhibit low quantum conversions (conversion of incoming photons to collected charges). Higher efficiencies were obtained by mixing the donor and acceptor moieties in a mixed-layer device. This led to the complication that the interfaces did not only consist of ITO/donor, donor/acceptor and acceptor/metal, but also of ITO/acceptor and donor/metal interfaces. Thus, Figure 1.1D does not describe the energy diagram for a mixed-layer device.

Furthermore, the oversimplified diagrams of Figure 1.1 do not take into account the molecular events[82] that might occur at the interfaces such as chemical reaction between the metal and the polymer, band bending[82,83] and energy level alignment.[84] The first event (chemistry) is often neglected, even though there is a body of evidence supporting the chemistry at the polymer-on-ITO interface[85] and metal-on-polymer interface.[86,87] The chemistry that occurs at the metal-on-polymer interface depends not only on the nature of the metal involved, but also on the cleanliness of both materials and the vacuum system used for the vapor deposition of the metal cathode. The deposition of aluminum atoms on polymer surfaces leads to cluster formation,[88] and to the formation of covalent bonds between Al and

the vinylene-carbon atoms of PPV.[89] Diffusion of the aluminum atoms is limited to the near-surface region and is localized in the first 20–30 Å. For calcium, it was observed clearly that the calcium atoms donate electrons to the first 20–30 Å of the PPV-layer, and form Ca^{2+} ions.[90] At the polymer-on-ITO interface, similar chemical reactions (oxidation of the PPV, diffusion of indium,[91] etc.) have been found to occur. Hence, chemically p-doped conjugated polymers are frequently used as hole injection electrodes, e.g. poly(dioxyethylene thienylene) (PEDOT) doped with poly(styrenesulphonic acid) (PSS), to provide a blocking layer for the chemical reaction of ITO with PPV.[26]

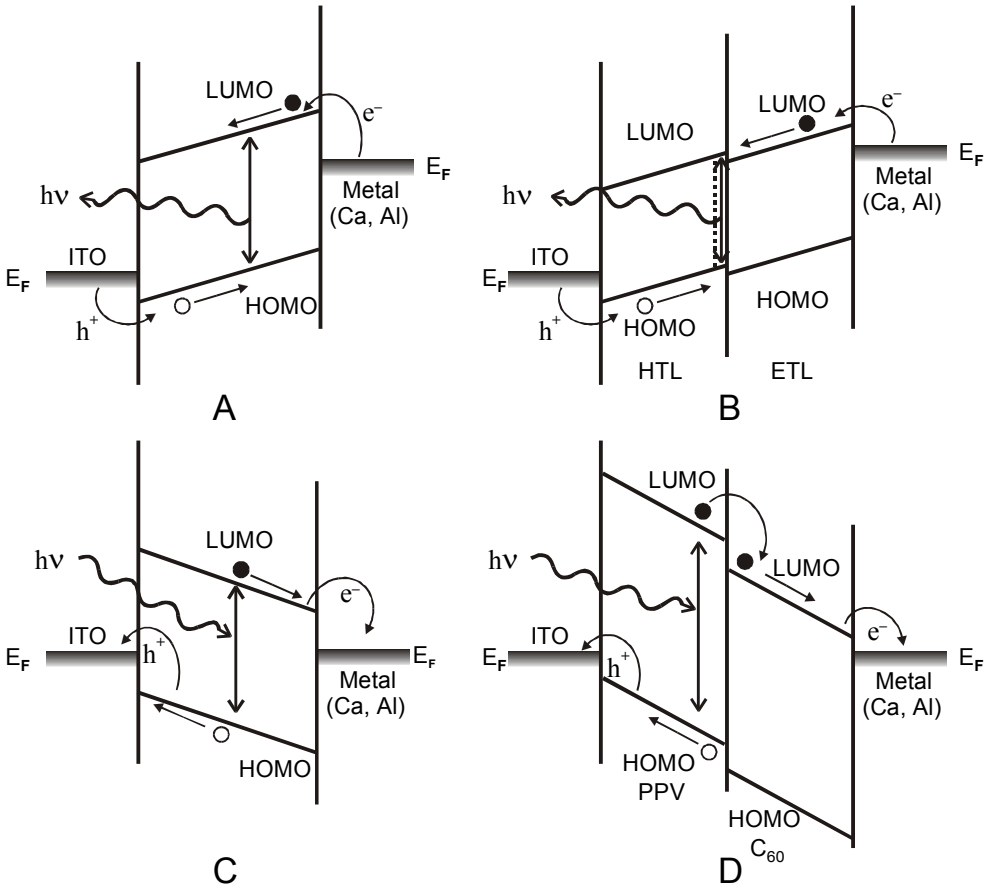

Figure 1.1 *Schematic energy diagrams of a single-layer organic LED (A), a double-layer LED where the dotted line indicates a recombination zone close to the interface (B), an organic single-layer PVD (C) and an organic double-layer PVD (D). The PVD energy diagrams are depicted under short-circuit conditions.*

Controlled chemical modifications of the inorganic surfaces can improve the device performance tremendously as demonstrated by the vapor deposition of a very thin layer (< 1 nm) of LiF before vapor-depositing the metal cathode.[20,92] As described above, the anode (ITO)/polymer interface can be easily modified by spin-coating a layer of p-doped conjugated polymer (PEDOT/PSS).[26,79] This high work function (~5.2 eV)[93] polymer electrode enhances the device uniformity and longevity due to its environmental stability.

A more sophisticated and elegant approach to chemically modifying surfaces and interfaces is demonstrated in Chapter 7, in which the formation of a chemically grafted monolayer that is capable of a "living" free radical polymerization, is described.[77] In this method, one covalently modifies the metal/polymer interface, and retains control of the layer thickness arising from that monolayer. This approach, when applied to monomers consisting of conjugated side-chains connected to a polymerizable end-group, might indeed result in control of the interfaces between the growing polymer film and the electrode.

1.5 Aim and outline of this thesis

Our goal is to develop novel, conjugated polymers, which are applicable in thin-film opto-electronic devices such as LEDs and PVDs. Our approach consists of implementing the functionalities, required for efficient performance, into one macromolecule that is constructed of two blocks. The electronic functions could be either in the main chain of the blocks or in substituents. Due to the chemical connectivity of the two blocks, they are forced to microphase separate on a nanometer scale. Microphase separation would produce a suitable geometry at the proper scale that could be fine-tuned via the lengths of the blocks. In this context, cylindrical and bicontinuous interpenetrating morphologies are the most appropriate ones. By utilizing "living" free radical polymerization techniques, the molecular weight and, therefore, the morphology, is controlled.

Each block exhibits specific functionalities that are designed for their specific device application. For LEDs, we designed and synthesized block copolymers consisting of a hole-transporting and highly fluorescent PPV moiety, and an electron-transporting block (oxadiazole-based). The design is such that the bipolar charge transport from the electrodes to the recombination zone is improved, resulting in balanced charge transport for EL. For the second application, that of PVDs, we designed and synthesized block copolymers in which one block exhibits the functionalities of light-absorber/exciton generator/hole conducter (PPV), and the other block acts as an electron acceptor/electron conductor (e.g. C_{60}-derivative).

A further aim is to study the influence of the structural conformation of the block copolymers in solution and the microphase separation/morphology in the solid-state on the final device performance. By simulating the casting conditions of the polymer in solution, and by investigating the local ordering in solution, a better understanding of the influence of the casting conditions on the final morphology can be obtained. Morphological

observations of the solid films can provide information on the local order of polymers and the influence of order on the device performance. Ultimately, this should lead to the establishment of relationships between thin-film structure/ordering and opto-electronic properties.

Chapter 2 describes the design and synthesis of a series of novel diblock copolymers, in which one block is PPV and the other is a C_{60}-functionalized polystyrene.[94,95] These semiconducting diblock copolymers are designed to be efficient photovoltaic materials with continuous and nanometer-scale interpenetrating phases of electron donor and acceptor components. The PPV block (rod) acts as the light-absorber and hole-conductor and the C_{60}-functionalized styrene block as an electron acceptor and electron conductor.

For the application in light-emitting diodes (LEDs), block copolymers were designed and synthesized consisting of a block based on PPV and a block based on oxadiazole side-chains. Besides block copolymers having PPV as the backbone, copolymers consisting of a block with oligo(*p*-phenylene vinylene) side-chains and a block with pendant oxadiazole units were synthesized.

During casting of soluble, semiconducting polymers, both the temperature and the quality of the solvent are strongly affected due to rapid evaporation of the solvent and the increasing concentration of the semiconducting polymer. The influence of the solvent temperature and the solvent quality on the chain conformation and the aggregation of semiconducting block copolymers[96] is described in **Chapter 3**.

In **Chapter 4** the thermotropic properties and the solid-state morphology of PPV-based block copolymers are studied. The corresponding homopolymer, poly(1,4-(2,5-dioctyloxy)phenylene vinylene), is liquid-crystalline and, consequently, the PPV-based block copolymers possess complex and rich phase behavior due to the combination of a mesogenic rod-like block and a flexible coil-like block. Elongated, lamellar-like microphases were observed for the semiconducting block copolymers.[96]

As demonstrated in **Chapter 5**, the covalent incorporation of C_{60} in the PPV-based block copolymer results in a strong quenching of the photoluminescence from the PPV block, which is indicative of an efficient electron transfer at the donor–acceptor interface.[94,96]

Furthermore, photovoltaic devices based on thin films of donor and acceptor moieties, either a blend of donor and acceptor homopolymers or a donor–acceptor block copolymer, were prepared. The donor–acceptor block copolymer demonstrated a superior photovoltaic response over the blend of the two constituent homopolymers, which is attributed to the smaller length scale of the phase separation in the block copolymer film.[96] This increases the donor–acceptor interface area relative to that of the blend and promotes the formation of continuous pathways for both holes and electrons.

In **Chapter 6**, the formation of highly ordered honeycomb structures upon drop-casting a solution of PPV-*b*-PS in CS_2 is described. The morphology of the honeycomb

structure consists of a two-dimensional array of spherical cavities with a diameter of 3–5 μm in a polymer film. This polymer film has an open structure showing holes with a diameter of 2–3 μm at the surface. This open structure was subsequently used as a template for the formation of a two-dimensional hexagonal array of functional dots, namely, aluminum cups.[97,98]

Chapter 7 describes a novel method to modify the surface properties of inorganic substrates by chemically grafting an initiator for "living" free radical photopolymerizations. The surface-grafted initiators were utilized for the controlled growth of homopolymers and block copolymer from the surface of the substrates and demonstrate an increase of the polymer layer thickness with time up to ~100 nm.[77] This method provides a novel approach to chemically modifying the surface between the active polymer and the electrodes in opto-electronic devices.

The design, synthesis, characterization and properties of regioregular, amphiphilic polythiophenes is described in **Chapter 8**. These polythiophenes form stable monolayers on the water subphase of a Langmuir trough and are transferable (Langmuir–Blodgett deposition) to solid substrates to give highly ordered thin films. Mixing of the amphiphilic, regioregular polythiophenes with a non-conducting poly(ethyleneglycol), in a 50/50 weight-% ratio, results in the formation of a semiconducting network of polythiophene in the Langmuir–Blodgett film.

The solution-cast films of the amphiphilic, regioregular polythiophenes exhibit liquid crystalline lamellar mesophases with thermotropic transitions at 0 °C, 60 °C and 120 °C. These transitions are attributed to the melting of the tetraethyleneglycol monomethyl ether side-chains, the dodecyl side-chains and the polythiophene backbones, respectively. DSC, X-ray diffraction and optical microscopy were used to identify the thermotropic transitions. The molecular ordering was investigated with X-ray and electron diffraction.[99]

1.6 References

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